Factors Governing Paint Consistency

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Factors Governing Paint Consistency[1]

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In this paper we have described the four factors on which the consistency of paint depends, more particularly the factor—flocculation in the pigment-vehicle system. Following a discussion of the force of flocculation, its influence on yield value and mobility, and the great change in paint consistency which can be brought about by a heavy bodied oil, such as poppyseed oil, we have tried to show whether or not it is possible for paints with the same yield value and mobility to have different consistencies. The value of such a study to paint technology has been pointed out.

THE FOUR FACTORS GOVERNING PAINT CONSISTENCY[2]

It has been shown that paint is not a truly viscous liquid, but instead a slightly plastic material;[3] further, it has been demonstrated that if its flow through a capillary tube could be maintained *completely telescopic* throughout the lowest pressures, then its pressure-rate-of-flow curve would be linear and intersect the pressure axis at the right of the origin[4] (Fig. 1). From these facts it follows that for a given paint there is a definite shearing stress below which telescopic flow cannot take place. This stress has been called the *yield value*. The slope of the curve, Fig. 1, is a function of the *mobility* of the paint; it may be considered as the reciprocal of *viscosity*, though it is not strictly correct to apply this term to plastic materials.[5]

All resistances to paint flow, regardless of their inception or manner of functioning, will be recorded either in the yield value or mobility, or jointly in both. On the basis of this, a tentative definition of paint consistency will be made: *The consistency of paint is that property imparted to it by virtue of its yield value and mobility.*

Before analyzing this definition, in order to ascertain if it is possible to have two paints of the same yield value and mobility and still recognize them as having different consistencies, it will be necessary to study the governing factors on which yield value and mobility depend. These factors are (1) the viscosity of the vehicle, (2) the pigment-vehicle ratio, (3) the force of flocculation in the pigment-vehicle system, (4) particle size of the pigment.

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[1] Received August 22, 1922. Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] The expression "paint consistency" refers to the consistency of *any* paint, whether it be good or poor; it is not to be confused with "painting consistency," which is simply a special case in which the consistency is considered right for painting purposes.

[3] Bingham and Green, *Proc. Am. Soc. Testing Materials*, 19 (1919), 640.

[4] Green, *Ibid.*, 20 (1920), 451.

[5] Bingham has given the name "rigidity" to the reciprocal of "mobility."

That the consistency of paint depends on (1) and (2) is self-evident and has always been so regarded. The importance of (3), however has been overlooked; and, as (4) is closely connected with (3), the real function of (4) has not been fully appreciated. In regard to (1), it will be shown that it is erroneous to suppose that in every case the more viscous the vehicle used, the less mobile the paint produced. Concerning (2), it is obvious that the yield value will vary directly and the mobility inversely as some function of the percentage pigment content. Experimental evidence of this has been given elsewhere.[4]

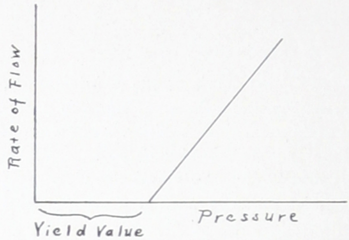

Fig. 1—Pressure-rate-of-flow curve for paint, assuming flow to be telescopic throughout entire range

PIGMENT FLOCCULATION

As (3) is one of the most important of the four factors, it is necessary to consider it in detail.

Definition of Flocculation

In order that no misunderstanding may arise as to the meaning of the term "flocculation," it must be realized that it is used in this paper in a particular sense, and under no circumstance will it be permissible to substitute any other picture or model of this condition of aggregation than the one given here. Admittedly, it is used in an arbitrary manner, for which an apology is unnecessary as there is no choice left in the matter to one who wishes to be perfectly definite in regard to this important phenomenon.

Flocculation is a condition of aggregation; it is that condition or state of affairs which has arisen when the dispersed phase ceases to be *uniformly* dispersed and exists in groups or clusters, the individual units (particles) of which are closely held together apparently by the residual surface tension existing in the interface between the dispersed and continuous phases.

When the word "flocculation" is used it implies three things: (1) a previous state having existed in which the discontinuous phase was dispersed in a continuous phase; (2) the units of the discontinuous phase brought into contact with each other (owing to convection currents, mechanically produced motion, etc.) forming groups (flocculates); and (3) adherence (apparently due to surface tension) of the touching units.

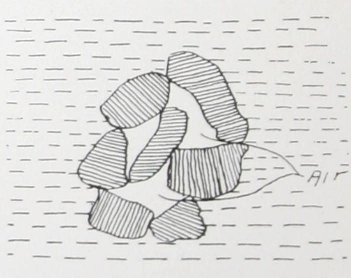

Fig. 2—Undispersed lump

Fig. 2 shows an undispersed lump of pigment immersed in a liquid vehicle. The vehicle is in contact only with the exterior of the lump; the interior contains air spaces. By mechanical means this lump is broken up and completely dispersed (Fig. 3). In this illustration the air spaces have been eliminated and the vehicle is presumably in complete contact with the surface of each particle. Assuming that gravity has no effect and there still remains a sufficient amount of surface energy in the pigment vehicle interface, then, if these particles are brought in contact with each other, they will loosely adhere (presumably owing to the surface energy), forming a flocculate (Fig. 4.) The intervening spaces between the pigment particles are now filled with the vehicle.

Furthermore, even between the apparent points of particle contact there probably exists a film of vehicle. There is no penetration of the vehicle into the intermolecular spaces of the particle. The particles do not get so closely together that they cohere, forming larger ones. Flocculates in no way behave as large individual particles.

The author has shown that under low pressures paint flow through a capillary is not telescopic, and, hence, the actual curve produced in practice is such as that shown in Fig. 5. By studying under the microscope the flow of paint through capillaries, it was possible to see that when low pressures were applied, corresponding to Branch *a*, internal telescopic shearing did not take place and the material (owing to slippage) moved in a solid mass (Fig. 6). This cessation of telescopic shearing was caused by the fact that the pigment was flocculated—a natural condition in paints—and that the force of flocculation was sufficient to hold the mass intact.[6] When sufficiently high pressures were applied, this force could be overcome, the material sheared, and Branch *b* of the curve produced (Fig. 7).

The upper branch of the curve was pushed away from the origin on account of the introduction of the lower one. If *a* had not been produced (in actual practice), *b* would have intersected the origin and the yield value would have been zero; but as *a* was caused mostly, if not entirely—as shown below—by flocculation, we are forced to the conclusion that yield value itself is due principally to the *force* of flocculation which holds the pigment particles together.

If Sulman's theory[7] is accepted as the explanation of flocculation, this force resides in the solid-liquid interface, and is due to incompleteness of wetting. The less the degree of wetting the greater the force of flocculation and consequently the greater the yield value.

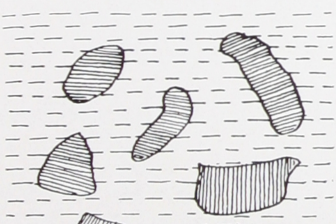

Fig. 3—Particles dispersed

In order to fully appreciate the importance of flocculation to paint consistency it is necessary to perform the following experiment:

Make up a semipaste of zinc oxide with either kerosene or Nujol (two poorly wetting oils). It will be noticed in the process of mixing vehicle and pigment, that an abnormal quantity of the liquid can be added without producing a mixture with a tendency to flow out under its own weight. This paste will be decidedly plastic and possesses a yield value. When the consistency is correct for the experiment, the mass should be sufficiently plastic to retain its form, as shown in Fig. 8. Now add a drop or two of *bodied* (heat-thickened or air-blown) poppy-seed oil and rub in well with a spatula. The effect is striking; the paste loses its yield value and becomes extremely fluid (Fig. 9). It no longer bears the slightest resemblance to its former consistency; in fact,

[6] The reason for the *gradual* discontinuance of telescopic flow under decreasing pressures is given by E. Buckingham, *Proc. Am. Soc. Testing Material*, 21 (1921), 1154.

[7] "A Contribution to the Sudy of Flotation," *Bull. Inst. Mining Metal.*, 182 (1919).

the entire range in consistency from one extreme to the other seems to have been passed through by the mere addition of but a few drops of heavy-bodied oil.[8]

This phenomenon is not a case of the fluidity of the added poppy-seed oil being so great as to cause a thinning of the mixture, for, in the first place, only a relatively small amount is added, and, secondly, the fluidity of this oil *is actually less* than the mobility of the mixture of zinc oxide and kerosene or Nujol. In other words, if it were to produce any effect at all, on the basis of this reasoning, it should be one of thickening rather than thinning of the paste. How, then, are we to arrive at a satisfactory explanation? With the knowledge that flocculation is the principal cause of yield value in paint, and that the degree of flocculation is a function of wetting of pigment with vehicle, it is not difficult to suppose that the poppy-seed oil has diminished the surface energy in the solid-liquid interface and thereby produced deflocculation.

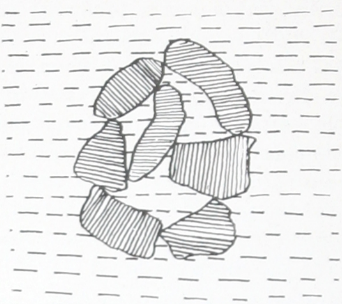

Fig. 4—Flocculate

The flocculated pigment is the "structure" which holds the mass together, giving it a plastic nature; when this structure is destroyed plasticity tends to vanish.

It is not necessary to remain content with this statement as a pure theory, for it is easily verified as a fact. Fig. 10 is a photomicrograph, under low power, of the zinc oxide and kerosene in its original state—that is, as a plastic material; Fig. 11 is the same after the addition of the poppy-seed oil; the first is flocculated and the second, deflocculated. Experimental data, taken with a Bingham and Green plastometer, on the mixtures of various pigments and oils before and after deflocculation, are given in Table I. It was necessary to make these mixtures fairly stiff in order to prevent the separation of pigment and vehicle during the running of the test, and hence they are not ideal for illustrating the fact that yield value can, under proper conditions, be reduced to a nearly negligible quantity by deflocculation. The best example is the Nujol-lithopone

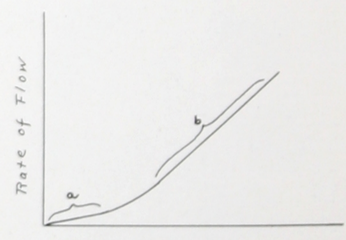

Fig. 5—Actual form or pressure-rate-of-flow curves produced in practice

[8] This experiment was first shown to the author by F. P. Ingalls.

mixture where the yield value drops from 3.77 to 0.054, the smaller quantity being scarcely measurable. In the case of the white leads with Nujol, and zinc oxide with linseed oil, wetting is fairly high to begin with; consequently, the effect of the poppy-seed oil is lessened. The residual yield values in these cases can be attributed either to imperfect deflocculation or frictional[9] resistance between the particles from close packing.

The importance of flocculation to the phenomenon of "oil absorption" should be apparent from a study of photographs (Figs. 8 and 9). Both mixtures possess practically the same pigment-vehicle ratio, but the pigment in Fig. 8 could be made to absorb many times its present volume of oil before it would assume the fluid appearance shown in Fig. 9. The flocculated mass acts like a sponge. The specific surface of the pigment—usually granted to be of major importance in oil absorption—is the same in both cases, and therefore cannot be regarded as the deciding factor.

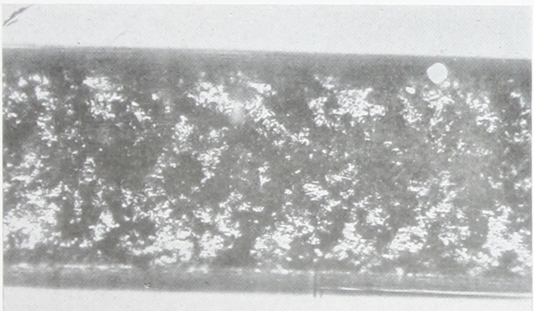

Fig. 6—Photomicrograph of paint in capillary tube. The pigment particles are flocculated and the flocculates interlocked, thus holding the mass intact under low pressures

EFFECT OF SIZE OF PARTICLE ON CONSISTENCY OF PAINT

It should now be possible to obtain a fuller understanding of the manner in which particle size of pigment affects the consistency of paint.

Let us consider two zinc oxide paints ground in the same vehicle and in the same proportions; further, let it be assumed that the degree of wetting is identical for both pigments. The only difference is to be one of particle size. Let the first one be a coarse-grained zinc oxide, and the second, a fine one. Bear in mind that when true flow takes place the flocculates are sheared; that the particles are thereby pulled away from the ones to which they were flocculated; and that a resistance to "pulling away" is set up, because of the surface energy residing in the interface. It is then clear that the more extensive the pigment surface per unit area

[9] E. C. Bingham, *Bur. Standards, Sci. Paper* 278.

of shearing surface, the greater will be the amount of surface energy created, and consequently the higher the yield value produced. As the finer oxide has the larger surface per given volume, it follows that it will give the higher yield value.

It is unnecessary to check this fact with measurements taken on the plastometer, for it becomes at once self-evident, when two such pigments are mixed with similar amounts of vehicle, that the finer grained one produces the stiffer (higher yield value) mass. Perhaps it cannot be emphasized too often that the only allowable difference here is that of particle size; and so one should not conclude that if two different pigments, zinc oxide and lithopone, for example, are identical in size, they will produce equal yield values if ground to the same pigment-vehicle ratio. Their degrees of wetting might be entirely different.

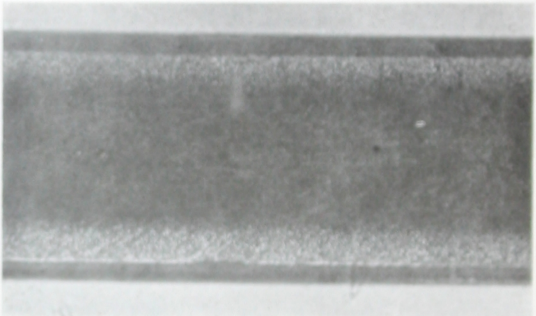

Fig. 7—Photomicrograph or paint in capillary tube under pressure sufficiently high to shear the flocculates. Complete telescopic flow has ensued

EFFECTS OF FLOCCULATION ON MOBILITY

So far no mention has been made of the effect of flocculation on mobility. It is comparatively easy to visualize a structure imparting a yield value—a definite stress below which the structure refuses to shear—to a paint, but its effect on mobility is less easily grasped. It is not difficult, however, to visualize this if we start reasoning at the correct place—with a viscous liquid. Qualified by suitable units of measurement, viscosity may be considered as the force required to maintain a stated relative uniform velocity between two shearing surfaces. It is necessary to apply a constant force because a constant resistance is offered. Any sudden alteration in the system causing an increase in resistance will demand a corresponding increase in the force applied, in order that the required velocity may not be impaired. The introduction of solid particles will do this; if these

particles flocculate, forming a structure, a still greater resistance is developed, and this must be met with a still greater applied force if the original (and required) velocity is to be maintained intact. Hence, flocculation should cause an increase in viscosity, or—more correctly speaking with regard to paints—a decrease in mobility.

Table I—Effect of Deflocculation on Yield Value and Mobility

	Yield Value	Mobility	Density	Temperature °C.
Nujol, B. C. W. L.	1.86	0.110	2.59	22.0
+				
Poppy-seed Oil	1.17	0.141	....	22.0
Nujol, S. W. L.	1.17	0.188	2.00	21.7
+				
Poppy-seed Oil	0.199	0.245	....	21.65
Nujol, Lithopone	3.77	0.202	1.23	21.8
+				
Poppy-seed Oil	0.054	0.529	....	21.8
Nujol, Zno	3.17	0.188	1.35	22.9
+				
Poppy-seed Oil	0.90	0.302	....	22.9
+				
Poppy-seed Oil	0.25	0.342	....	22.85
Raw Linseed Oil, ZnO	1.56	0.403	1.83	21.9
+				
Poppy-seed Oil	0.857	0.465	....	21.9
KAPXX, Acid No. 6, ZnO	3.17	0.238	2.02	22.0
+				
Poppy-seed Oil	2.57	0.261	....	22.0
Poppy-seed Oil: Fluidity (Mobility)	0.0792			
Poppy-seed Oil: Viscosity	0.00126			
Poppy-seed Oil: Temperature, °C	21.9			

In order to secure experimental evidence that this line of reasoning has led to a correct conclusion, it is necessary to work with a system in which it is possible to alter the state of flocculation without appreciably changing its composition. This is accomplished most successfully by working with mixtures of either lithopone or zinc oxide and Nujol, where the effects of deflocculation can be exaggerated. The method, of course, is by working backwards—i. e., starting with a flocculated mixture, measuring its mobility, deflocculating with poppy-seed oil, measuring again and noting the difference, if any. Table I records the data of this series of experiments. It will be observed that in each case deflocculation causes an *increase in mobility;* this is tantamount to a decrease of mobility on flocculation.

VALUE TO PAINT TECHNOLOGY

We are now in a position to realize the value that the study of flocculation is to paint technology. It has been shown that flocculation materially influences both mobility and yield value, and that these in turn define paint consistency. This fact alone is of great importance, but perhaps

even greater is the radical change that can be produced in consistency by the application of literally homeopathic doses of a heavy-bodied oil. Poppy-seed oil is by no means the only oil that is capable of introducing this change, for, in fact, nearly any properly bodied vegetable oil possesses this property to some extent. For this reason we cannot always assume that, of two paints, the one containing the more viscous vehicle will necessarily be the less mobile, because very viscous oils are often good deflocculators, and it would be conceivable that such a paint might even be more mobile than one formed from a less viscous but strongly flocculating oil.

It might be worth while mentioning, at this point, that the thinning of paints, either shortly after application and before drying, or while still in the container, is probably due to an increase in wetting power of the vehicle arising from the absorption of oxygen, most likely from the surface of the pigment itself. Increased wetting causes deflocculation, which in turn destroys the yield value of the paint, enabling it to flow easily under its own weight.

Fig. 8

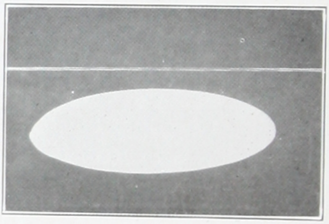

Fig. 9

Fig. 8—Plastic mixture of zinc oxide and kerosene. Particles flocculated

Fig. 9—After the addition of a small amount of poppy-seed oil. Particles deflocculated

Fig. 12 shows the effect on the plastic flow curve of simple deflocculation—a decrease in yield value plus an increase in mobility. Fig. 13 shows the result from oxidation. If oxidation is slight it should produce practically the same effect as illustrated in Fig. 12, for oxidation increases wetting; on the other hand, if the absorption of oxygen continues until the vehicle becomes *extremely* viscous, then the mobility of the paint will fall. Paradoxically, such a paint has thinned and thickened at the same time. In the case of soap formation, we have simply the addition of new particles, either colloidal or crystalloidal, and perhaps the removal of a certain percentage of the finest of the pigment particles. The net result is likely to be an increase in the total number of particles, which produces the same effect as increasing the pigment-vehicle ratio—i. e., a raising of the yield value and a lowering in mobility.

The object of this paper has been to discuss the four *cardinal* factors controlling paint consistency. Naturally there are others, such as temperature, for instance, but this may be called a minor one, for no investigator is liable to judge consistency at any temperature that varies radically from normal room temperature; hence, the range is small and the effect of secondary importance. Soap formation has a pronounced influence on paint consistency, but this, in most cases, can be considered as a subdivision of factor (2) or (4).

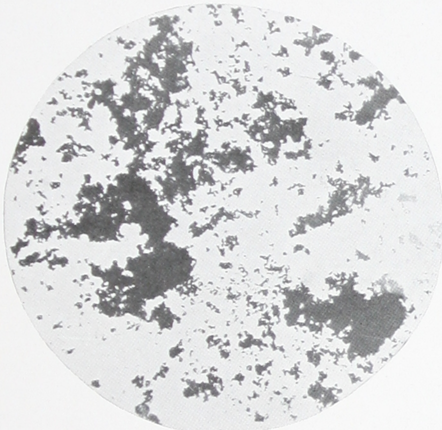

Fig. 10—Photomicrograph of the plastic mixture shown in Fig. 8. Particles flocculated into dense masses

PROBLEMS OF GELATINIZATION AND STRINGINESS

It is now necessary to consider the question raised in the opening paragraphs. Is it possible to have two paints possessing identical yield values and mobilities, and at the same time recognize them as having different consistencies? As pointed out, all resistances to flow are recorded in the yield value and mobility; but do these quantities express such anomalies sometimes occurring in paint, as gelatinization and stringiness? It is certainly proper and permissible to speak of gelatinous and stringy consistencies. The phenomenon of gelatinization may manifest itself in two ways—either the vehicle gelatinizes or the pigment particles become covered with soap, firmly binding them together into an elastic mass. In both cases structure is formed which would increase the yield value and decrease the mobility. An attempt to secure measurements with the plastometer would only result in the breaking of this structure, which was a matter of slow growth, and hence it is problematical whether or not

the readings would be true values. Therefore, it will be a difficult matter to decide, from experimental evidence, if gelatinization is defined by and incorporated in the figures given by yield value and mobility. It might be well to point out that flocculates themselves are always dispersed during their passage through the capillary tube, but it is not actually the existence of the flocculates that influences yield value and mobility, but the *force* of flocculation, and this remains intact as long as the wetting properties of pigment and vehicle are unaltered.

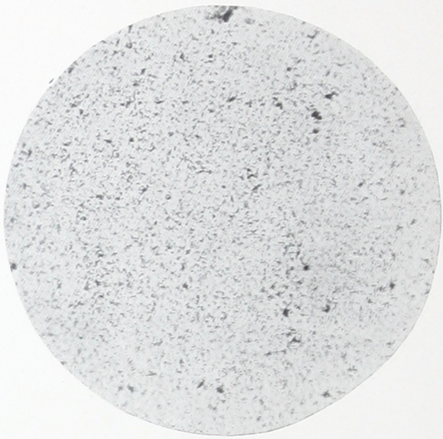

Fig. 11—Photomicrograph showing completeness of deflocculation after addition of poppy-seed oil

If it should become possible to simulate gelatinization by a proper combination of the four governing factors, then certain yield values and mobilities would result that would henceforth be indicative of this type of consistency. Furthermore, if these yield values and mobilities should happen to match those of a truly gelatinized paint, then the tentative definition of paint consistency would be immune from attack as far as gelatinization is concerned.

At first glance these suppositions seem far removed from the realm of possibility, but deeper reflection will instill caution against arriving at a hasty and doubtful conclusion; it will develop the realization of the existence of undiscovered and latent possibilities, and emphasize the extreme difficulty of visualizing the mechanism of a model possessing the properties of a gelatinous paint. At

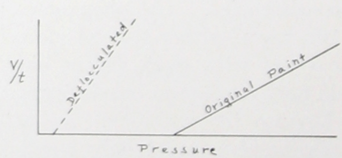

Fig. 12—The effect of deflocculation on yield value and mobility, shown graphically

present no one has produced any evidence indicating that the idea of simulating gelatinization is untenable, and so the question remains an open one from this aspect.

In regard to stringiness of paints, the author believes that this depends on the fulfilment of four basic conditions: (1) comparatively high viscosity of vehicle, (2) pigment deflocculated, (3) pigment particles relatively fine, and (4) low surface tension of vehicle against air. Care must be taken to recognize an essential distinction—that the fulfilment of these conditions will not necessarily produce stringiness, but if stringiness *is* to be produced, then these four conditions must be maintained. For instance, an ordinarily high pigment-vehicle ratio could destroy stringiness, even though the four conditions were entirely satisfied.

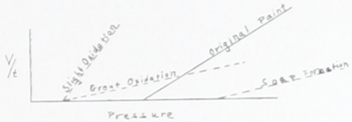

Fig. 13—The effect of oxidation and soap formation on the plasticity of paints

It will be observed that the first three requirements directly govern yield value and mobility, and, if it were not for the fourth, stringiness might be indicated in the measurements of paint consistency. If, however, a fundamental relationship exists between surface tension of vehicle against air and vehicle against pigment, then the fourth condition would be a function of flocculation and could not be raised as an objection to the definition. Fortunately, whether this relationship exists or not, the range of variation in surface tension of the highly viscous paint vehicles is narrow, and it would seem, from a practical viewpoint, to be impossible to produce two paints of equal yield values and mobilities, one of which is stringy and the other not.

In view of these considerations, the author feels that the definition of paint consistency may be accepted without qualification, at least until there are considerably more experimental data on gelatinization and stringiness available for study than at present.

May 15, 1923.